Using modern low-oxygen marine ecosystems to understand the nitrogen cycle of the Paleo- and Mesoproterozoic oceans

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Significance Statement

This review combines data from modern Oxygen Minimum Zones and data from the marine sedimentary rock record, bringing together two disparate communities and providing a new perspective on the Proterozoic ecosystem.

Summary

During the productive Paleoproterozoic (2.4-1.8 Ga) and less productive Mesoproterozoic (1.8 to 1.0 Ga), the ocean was suboxic to anoxic and multicellular organisms had not yet evolved. Here we link geologic information about the Proterozoic ocean to microbial processes in modern low oxygen systems. High iron concentrations and rates of Fe cycling in the Proterozoic are the largest differences from modern oxygen deficient zones. In anoxic waters, which composed most of the Paleoproterozoic and ~40% of the Mesoproterozoic ocean, nitrogen cycling dominated. Rates of N_2 production by denitrification and anammox were likely linked to sinking organic matter fluxes and in situ primary productivity under anoxic conditions. Additionally autotrophic denitrifiers could have used reduced iron or methane. 50% of the Mesoproterozoic ocean may have been suboxic, promoting nitrification and metal oxidation in the suboxic water and N_2O and N_2 production by partial and complete denitrification in anoxic zones in organic aggregates. Sulfidic conditions may have composed ~10% of the Mesoproterozoic ocean focused along continental margins. Due to low nitrate concentrations in offshore regions, anammox bacteria likely dominated N_2 production immediately above sulfidic zones, but in coastal regions, higher nitrate concentrations probably promoted complete S-oxidizing autotrophic denitrification at the sulfide interface.

Introduction

The last two decades have witnessed ever more refined studies of biogeochemical cycles on the Precambrian Earth with expanding applications of novel isotopic proxies (Kendall *et al.*, 2017; Stüeken, 2017; F. Zhang *et al.*, 2020) and increasingly sophisticated computational models (Olson *et al.*, 2013; Reinhard *et al.*, 2016; Laakso and Schrag, 2017). These studies have uncovered temporal and spatial nuances in seawater oxygenation and revealed feedbacks between tectonic, climatic and biological processes (Mills *et al.*, 2014; Lee *et al.*, 2016; Husson and Peters, 2017). At the same time, oceanographers and microbiologists have been advancing our understanding of the marine nitrogen cycle in a range of redox conditions that are analogous to the early Earth (Babbin *et al.*, 2014; Devol, 2015; Bristow *et al.*, 2016; Oschlies *et al.*, 2019). However, linkages between the two communities of researchers are rare (Michiels *et al.*, 2017; Schad *et al.*, 2019). Here we bridge this gap with a review of modern nitrogen metabolisms linked to Earth's environmental history over geologic timescales.

The redox evolution of Earth's ocean and atmosphere

The emergence of cyanobacteria capable of performing oxygenic photosynthesis >3.0 billion years ago (Ga) (Planavsky, Asael, *et al.*, 2014) has profoundly impacted the evolution of biogeochemical cycles. However, the transition towards a fully oxygenated world unfolded slowly over geologic time (Figure 1). Until the end of the Archaean (4.0-2.5 Ga), Earth's ocean and atmosphere were largely anoxic (Lyons *et al.*, 2014). Evidence for this view comes from photochemically-produced mass independent fractionation of sulfur isotopes in Archaean sedimentary rocks (Farquhar *et al.*, 2001). This signal is erased by small oxygen concentrations, indicating that the atmosphere contained < 1ppm O_2 until the beginning of the Paleoproterozoic around 2.4-2.3 Ga (Farquhar *et al.*, 2001; Pavlov and Kasting, 2002; Guo *et al.*, 2009). Under these anoxic conditions, methane was probably more stable in the atmosphere and may have contributed to greenhouse warming (Haqq-Misra *et al.*, 2008; Laakso and Schrag, 2019). Oceanic iron concentrations, specifically ferrous iron, were likely much higher in the Archaean than today, as evidenced by abundant banded iron formations (James and Trendall, 1982; Konhauser *et al.*, 2017). Ocean waters were thus ferruginous. Some of this ferrous iron likely fuelled anoxygenic photosynthesis, called photoferrotrophy, which may have been the main mechanism for driving iron oxidation in the Archean (Widdel *et al.*, 1993; Kappler and Pasquero, 2005; Crowe *et al.*, 2008; Butterfield, 2015; Camacho *et al.*, 2017; Thompson *et al.*, 2019). Cyanobacteria probably produced oxygen in the marine euphotic zone, and, at least during the late Archaean, may have created "oxygen oases" in surface waters (Koehler *et al.*, 2018) as well as temporary whiffs of oxygen in the atmosphere (Anbar *et al.*, 2007). Microbial mats on land may have contained oxygen-producing cyanobacteria as well (Lalonde and Konhauser, 2014), which could have created a small flux of fixed nitrogen and oxidized sulfur to the ocean (Stüeken *et al.*, 2012; Thomazo *et al.*, 2018). It is thought that reservoirs of reduced species (iron, sulfur, carbon and hydrogen) at the Earth's surface had to be either oxidized by oxygen, buried in the mantle, or lost to space before free O_2 gas could build up in the atmosphere (Catling, 2014).

The Paleoproterozoic (2.4-1.6 Ga) saw the rise of atmospheric oxygen, perhaps even briefly up to modern levels (Bekker and Holland, 2012; Partin *et al.*, 2013). The presence of oxygen likely placed a strong upper limit on the greenhouse gas methane, potentially causing the global glaciations documented from the Paleoproterozoic (Haqq-Misra *et al.*, 2008; Olson *et al.*, 2016; Gumsley *et al.*, 2017). Higher oxygen levels likely also spurred the oxidation of pyrite on land, releasing sulfuric acid (Konhauser *et al.*, 2011), which would have both added sulfur to the ocean (Blättler *et al.*, 2018) and decreased the pH of soils (Konhauser *et al.*, 2011). It has been proposed that acidic waters may have resulted in a enhanced phosphorus release from apatite on land, which could explain the first occurrences of large phosphorite deposits at this time (Bekker and Holland 2012). Weathering rates may have been

twice as high as today (Bekker and Holland, 2012). This increase in the essential nutrient phosphate may have enhanced biological productivity in the ocean and caused intense organic carbon burial, consistent with a large positive excursion in carbon isotopes seen in the later part of the Paleoproterozoic (Lomagundi-Jatuli event, 2.3-2.1 Ga; Martin *et al.*, 2013). During the Paleoproterozoic, the deep ocean may have experienced at least brief episodes of oxygenation between 2.0-1.85 Ga (Kipp *et al.*, 2017, 2020; Planavsky *et al.*, 2018; Mänd *et al.*, 2020), but it likely returned to a mostly anoxic state after this interval (Kendall *et al.*, 2011). Incomplete oxygenation of the ocean at this time may place an upper limit on atmospheric oxygen levels (Kipp *et al.*, 2017). Alternatively, it is possible that warm temperatures before and after glacial events prevented efficient mixing of the water column, or that the flux of reductants from volcanic activity on the seafloor acted as a strong oxygen sink (Ossa *et al.*, 2018). Marine cyanobacteria were probably the main photosynthesizers in the Paleo- and Mesoproterozoic, although anoxic photosynthesizers using reduced iron or sulfide could also have played a role, particularly deeper in the photic zone close to the interface between oxic surface waters and anoxic deep waters (Johnston *et al.*, 2009; Butterfield, 2015; Camacho *et al.*, 2017; Thompson *et al.*, 2019). While modern unicellular cyanobacteria (*Synechococcus* and *Prochlorococcus*) probably did not evolve until the Neoproterozoic (Sánchez-Baracaldo, 2015), unicellular cyanobacteria did exist in the Paleo- and Mesoproterozoic and would likely have filled their niche (Butterfield, 2015).

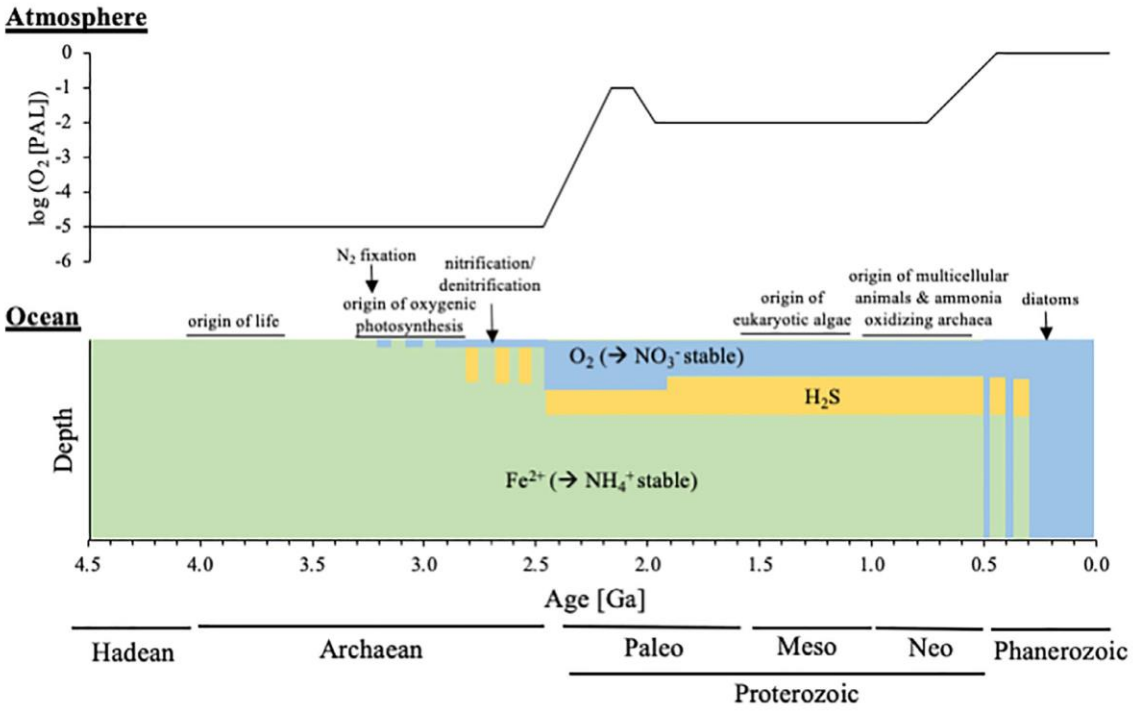

Figure 1: *Timeline of earth's history with atmospheric oxygen concentrations in PAL (present atmospheric levels) indicated in the upper panel and oceanic chemistry indicated in the lower panel. Green, yellow and blue indicate ferruginous, sulfidic, and oxygenated conditions respectively. Important events in organism evolution are indicated.*

Throughout the Mesoproterozoic (1.6 - 1.0 Ga), the deep ocean continued to be dominated by ferruginous (Fe^{2+}-rich) conditions (Planavsky *et al.*, 2011; Poulton and Canfield, 2011; Sperling *et al.*, 2015) while the surface ocean and atmosphere were oxygenated (Hardisty *et al.*, 2017). Temperatures were temperate during this interval with no evidence of glaciations, although the mechanism to maintain these warm temperatures is still debated (Buick, 2007; Roberson *et al.*, 2011; Olson *et al.*, 2016; Zhao *et*

al., 2018). Oxygen concentrations in the atmosphere for the Mesoproterozoic are controversial. While some datasets are consistent with as little as 0.1% of present atmospheric levels (Planavsky, Reinhard, *et al.*, 2014; Planavsky *et al.*, 2020), others suggest 1-10% (Daines *et al.*, 2017). It is also conceivable that oxygen levels were variable through time and space (Diamond and Lyons, 2018; Shang *et al.*, 2019; Steadman *et al.*, 2020). The oxygen concentrations could have decreased from the Paleoproterozoic to the Mesoproterozoic due to weathering of organic rich sedimentary rocks deposited during the Lomagundi-Jatuly event at the end of the Paleoproterozoic (Kump *et al.*, 2011) and then stayed low due to reduced weathering in a negative feedback loop (Daines *et al.*, 2017). Productivity estimates from sulfate ^{17}O isotopes indicate that productivity rates may have been as low as 6% of modern levels during the Mesoproterozoic (Crockford *et al.*, 2018), possibly due to severe phosphorus limitation (Reinhard *et al.*, 2017). Phosphorus is scavenged by iron-carbonate minerals under ferruginous conditions (Derry, 2015). Coupled chromium and molybdenum data indicate that at least 30-40% and possibly as much as 100% of the deep ocean was anoxic and mostly ferruginous during this time, and up to 10% of seafloor was covered by euxinic waters (anoxic with >11 μM free H_2S) compared to 0.1% today (Reinhard *et al.*, 2013). This redox landscape thus greatly limited the marine P reservoir and suppressed productivity. The sulfidic waters probably extended mostly as wedges in upwelling zones along outer continental shelves above ferruginous bottom waters (Poulton *et al.*, 2010) (Figure 1). In such upwelling regions, nutrient availability would have been highest. The mechanism for this midwater sulfide zone is thus probably similar to that creating midwater oxygen minimum zones in the modern ocean (Lyons *et al.*, 2014). Aerobic degradation of organic particulates is highest in the upper ocean, thus oxygen is depleted in intermediate waters. However, the sinking flux is still significant, and because in the Proterozoic O_2 was not replenished by upwelling of oxic waters – as is the case today – conditions became highly anoxic at mid-depth. In deep waters, the sinking flux of organic matter was probably largely attenuated, such that conditions "relaxed" from euxinic to ferruginous.

Atmospheric oxygen levels likely rose to modern levels in the Neoproterozoic (1.0 to 0.54 Ga; Shields-Zhou *et al.*, 2011) or mid-Paleozoic (0.54-0.25 Ga), following the rise of land plants (Lenton *et al.*, 2016; Krause *et al.*, 2018) and the expansion of burrowing organisms and planktonic algae (Lu *et al.*, 2018; Tarhan, 2018). Until then, at least parts of the deep ocean likely continued to be anoxic and ferruginous with occasional euxinic intervals (Stockey *et al.*, 2020).

Precambrian records of the biogeochemical nitrogen cycle

Geochemists commonly use nitrogen isotopic ratios preserved in sedimentary rocks to determine which N cycling metabolisms were active in the past (reviewed by (Ader *et al.*, 2016; Stüeken *et al.*, 2016)). The two stable isotopes of nitrogen (^{15}N and ^{14}N) are fractionated by several permil during most metabolic pathways, and the biomass of living organisms that gets buried in sediments preserves $^{15}N/^{14}N$ ratios (expressed as $\delta^{15}N$ [‰] = $(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{air} - 1$) characteristic of its major N source. An important aspect to keep in mind when interpreting these records is that nitrogen is mobile during diagenesis. Measured $^{15}N/^{14}N$ ratios in rock samples therefore typically capture a bulk average value of all biomass present in the sample, meaning that only the most dominant N metabolisms are preserved. Intricate metabolic networks remain elusive.

When applied to sedimentary rocks from the Archean, this approach revealed $\delta^{15}N$ values around 0‰, consistent with significant degrees of biological N_2 fixation (Stüeken *et al.*, 2015). Importantly, the predominant enzyme appears to have been molybdenum-iron nitrogenase; alternative nitrogenases based on Fe or V impart larger fractionations (Zhang *et al.*, 2014) that are inconsistent with the Archean record (Stüeken *et al.*, 2015). This result is interesting since Mo concentrations were significantly lower in the Archean and Proterozoic due to widely anoxic conditions (5-10 nM instead of 105 nM; Reinhard *et al.*, 2013) whereas oceanic iron concentrations were much higher than today (0.1-1 mM instead of ~1 nM; Holland, 1984; Derry, 2015; Tosca *et al.*, 2016). However, the molybdenum-iron nitrogenase is significantly more efficient than alternative nitrogenases (Eady, 1996), and even low Mo levels are

sufficient to support at least low rates of N_2 fixation in modern organisms (Zerkle *et al.*, 2006; Glass *et al.*, 2009), and it is conceivable that early diazotrophs were adapted to lower Mo concentrations. Hence microbial metabolisms have likely been capable of transforming atmospheric N_2 into ammonium since the early Archean (Stüeken *et al.*, 2016).

In the late Archaean, nitrogen stable isotopes started to show more variability. Negative $\delta^{15}N$ values, which would indicate partial ammonium assimilation, are restricted to few sites in the late Archaean (Yang *et al.*, 2019), indicating that dissolved ammonium levels were usually below a few µM in the global ocean (Stüeken *et al.*, 2016; Koehler *et al.*, 2019). Rocks from around ~2.6 Ga show a 6‰ increase in the $\delta^{15}N$ of kerogen, indicating that light N was preferentially lost from the ocean, which is most parsimoninously explained by nitrate reduction to N_2 gas (denitrification), similar to the modern ocean (Godfrey and Falkowski, 2009; Koehler *et al.*, 2018). Denitrification requires the presence of nitrate, which in turn requires the presence of oxygen to oxidize ammonium (nitrification). These data are thus consistent with at least transiently oxic conditions in the surface ocean at that time. Positive $\delta^{15}N$ values became more widespread in Paleoproterozoic marine sedimentary rocks, indicating that denitrification (and by extension nitrate) became widely bioavailable during that time period (Zerkle *et al.*, 2017; Kipp *et al.*, 2018; Luo *et al.*, 2018; Cheng *et al.*, 2019). In contrast, during the Mesoproterozoic when oxygen concentrations were perhaps again slightly lower, positive $\delta^{15}N$ values are restricted to a few basins, and often to shallow-marine settings (Stüeken, 2013; Koehler *et al.*, 2017; Wang *et al.*, 2020). This patterns has been interpreted as a gradient in seawater nitrate levels from onshore (high) to offshore (low). Several perturbations in $\delta^{15}N$ are recorded in the Neoproterozoic and throughout the Phanerozoic, possibly driven by a combination of redox changes, biological evolution and global climatic shifts (Ader *et al.*, 2014; Algeo *et al.*, 2014; Johnson *et al.*, 2017; Wang *et al.*, 2018).

Although a billion years of evolution has occurred since the Paleo- and Mesoproterozoic, the geological record suggests that biological N_2 fixation, ammonium assimilation, nitrification and denitrificaiton, *i.e.* the major metabolic pathways that close the nitrogen cycle, had evolved by the Proterozoic (Figure 1). However, it is important to stress that sedimentary $\delta^{15}N$ of ancient biomass cannot distinguish between canonical denitrificaiton (nitrate reduced to N_2 coupled to oxidation of organic matter, ferrous iron or sulfide), anaerobic ammonium oxidation (anammox, which couples nitrate reduction to ammonium oxidation) and dissimilatory nitrate reduction to ammonium (DNRA). Isotopic fractionations imparted by these three pathways are too similar. To elucidate this knowledge gap and to provide better constraints on interpretations of ancient nitrogen isotope records, we combine information about carbon and nitrogen cycling and microbial ecology of modern low oxygen regions with our knowledge of the Paleo- and Mesoproterozoic.

Sources and sinks of nitrogen in the modern ocean

The major source of fixed nitrogen is biological N_2 fixation, which is mostly carried out by cyanobacteria in the photic zone (Montoya *et al.*, 2004; Moisander *et al.*, 2010; Zehr, 2011). In anoxic waters where sulfide is present, such as in the Black Sea or the Baltic Sea, anaerobic organisms such as sulfate reducers or S oxidizers are the major N_2 fixers (Fernandez *et al.*, 2011; Farnelid *et al.*, 2013; Kirkpatrick *et al.*, 2018) and at methane seeps, methanogens can be the main N_2 fixers (Dekas *et al.*, 2009). It is not known which organisms were the major diazotrophs in the Precambrian, but these modern observations from anoxic zones support the inference that the evolution of cyanobacteria was not a necessary requirement for wide-spread N_2 fixation. Fixed nitrogen is converted to ammonium during biomass degradation, and ammonium is stable in anoxic waters (Brewer and Murray, 1973). However, in the modern oxic ocean, most dissolved nitrogen is present in the form of nitrate.

Nitrate is formed by the sequential processess of ammonium oxidation and nitrite oxidation by specific chemoautotrophs, which can proceed at low oxygen concentrations down to a few nM (Lipschultz *et al.*, 1990; Bristow *et al.*, 2016). Ammonium and nitrite oxidation do need ammonium to

be produced from organic matter remineralization. In the modern oxic ocean, these chemoautotrophs fix ~10^{13} mol of organic C per year and thus are a significant source of organic carbon to the ecosystem (Y. Zhang *et al.*, 2020). The half saturation constant (K_m) for nitrite oxidation at low oxygen is 0.5 ± 4.0 nM O_2 (from two component fitting), which implies that nitrite oxidation can occur at oxygen concentrations below our ability to measure oxygen (Bristow *et al.*, 2016). Stable $\delta^{15}N$ and $\delta^{18}O$ isotopes indicate that both nitrite oxidation and dentrification occur in ODZs (Gaye *et al.*, 2013; Buchwald *et al.*, 2015; Peters *et al.*, 2016; Martin and Casciotti, 2017). Shipboard nitrite oxidation rates have been measured from oxygen deficient waters, and anaerobic nitrite oxidation through an unknown mechanism has even been proposed (Babbin *et al.*, 2017, 2020; Sun *et al.*, 2017, 2019). However, oxygen contamination at subnanomolar concentrations is quite difficult to avoid in experiments, so the mechanism involved in this oxidation remains elusive.

Ammonium oxidation to nitrite can be mediated by ammonia oxidizing archaea (Thaumarcheota) or ammonia oxidizing bacteria. However, the vast majority of ammonium oxidation in the modern marine water column is mediated by archaea (Martens-Habbena *et al.*, 2015; Peng *et al.*, 2015; Horak *et al.*, 2018) because these organisms have a greater ability to scavenge low concentrations of ammonium (Martens-Habbena *et al.*, 2009). For ammonia oxidizing archaea the half saturation constant (K_m) for oxygen is 333 ± 130 nM O_2 (Bristow *et al.*, 2016), preventing oxic ammonium oxidation from occurring in anoxic ODZs, where oxygen is <10 nM (Revsbech *et al.*, 2009), but allowing it in suboxic waters, where oxygen is <10 μM. Ammonia oxidation in the oxycline surrounding ODZs was mediated by archaea (Peng *et al.*, 2015). In suboxic regions above sulfidic zones, where ammonium fluxes are high (Fuchsman *et al.*, 2008), both archaea and bacteria have been implicated in ammonia oxidation (Lam *et al.*, 2007; Cernadas-Martín *et al.*, 2017). Ammonium oxidation by either archaea or bacteria produces N_2O as a by-product under low oxygen conditions; however ammonium oxidation by cultured proteobacteria (Goreau *et al.*, 1980; Kozlowski, Kits, *et al.*, 2016) produce at least ten fold more N_2O yield under low oxygen conditions than natural populations of archaea (Hink *et al.*, 2017; Ji *et al.*, 2018). The conversion from NO to N_2O is enzymatic in some ammonia oxidizing bacteria but abiotic in others and is abiotic for ammonia oxidizing archaea (Kozlowski, Kits, *et al.*, 2016; Kozlowski, Stieglmeier, *et al.*, 2016). Horizontal gene transfer from bacteria was probably necessary for Thaumarcheota to adapt from hyperthermophilic ancestors to the cold deep ocean (Brochier-Armanet *et al.*, 2011), and it is thought that Thaumarcheota did not spread to the marine environment until the Neoproterozoic (Ren *et al.*, 2019). Hence, unlike the modern ocean, bacteria likely mediated ammonium oxidation during the Paleo- and Mesoproterozoic. Bacterial ammonia oxidizers need higher concentrations of ammonium than do ammonia oxidizing archaea. The ability to scavenge low concentrations of ammonium may not necessarily have been evolutionarily advantageous in the Proterozoic, when the deep ocean was anoxic and ammonium-rich compared to today (up to ~10 μM; Stüeken *et al.*, 2016; Koehler *et al.*, 2019). Ammonia oxidizing bacteria are found in several distinct groups of bacteria including betaproteobacteria, gammaproteobacteria and Nitrospirae, though ammonium oxidizing Nitrospirae have not been found in the marine environment (Kits *et al.*, 2019). Since N_2O yields for beta and gammaproteobacteria are high (Goreau *et al.*, 1980; Kozlowski, Kits, *et al.*, 2016), we predict that the ancestral ammonia oxidizing bacteria produced significant amounts of N_2O under suboxic conditions in the Proterozoic.

There are three known and potentially competing pathways that lead to loss of fixed nitrogen from the ocean (which today is mostly in the form of nitrate): heterotrophic denitrification, autotrophic denitrification, and anammox. In both heterotrophic and autotrophic denitrification, nitrate is reduced using the same pathway.

$NO_3^- \rightarrow NO_2^- \rightarrow NO_{(g)} \rightarrow N_2O_{(g)} \rightarrow N_{2\,(g)}$

Heterotrophic denitrifiers use organic carbon as their reductant and have been preferentially found in particles suspended in the marine water column (Ganesh *et al.*, 2014, 2015; Fuchsman *et al.*, 2017). Autotrophic denitrifiers use ferrous iron (He *et al.*, 2016), methane (Ettwig *et al.*, 2010; Thamdrup *et al.*, 2019) or sulfur compounds such as hydrogen sulfide, elemental sulfur and thiosulfate (Takai *et al.*,

2006). S-oxidizing autotrophic denitrifiers have been found together with sulfate reducers in particles in non-sulfidic conditions (Fuchsman, Murray, *et al.*, 2012; Fuchsman *et al.*, 2017; Saunders *et al.*, 2019) and in the water column at sulfide interfaces (Hannig *et al.*, 2007; Jensen *et al.*, 2009; Lavik *et al.*, 2009; Fuchsman, Murray, *et al.*, 2012). Autotrophic denitrification with methane has also been found in anoxic waters (Ettwig *et al.*, 2010; Thamdrup *et al.*, 2019). All of these reductants (organic matter, methane, reduce sulfur, ferrous iron) would have been present in the anoxic Precambrian ocean, meaning that denitrification is unlikely to have been starved of reductant. Anammox is an autotrophic process where $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$ via a hydrazine intermediate with no N_2O produced (van de Graaf *et al.*, 1996, 1997). Anammox bacteria, known to be slow-growing (Strous *et al.*, 1999), have been found to have a free-living lifestyle in anoxic marine water columns (Fuchsman, Staley, *et al.*, 2012; Ganesh *et al.*, 2014). They may thus have been present along with denitrifiers in the Proterozoic ocean.

In all three major marine oxygen deficient zones (ODZs), the Arabian Sea, the Eastern Tropical North Pacific (ETNP) and the Eastern Tropical South Pacific (ETSP), heterotrophic denitrification and anammox rates significantly increased with the addition of sterilized sediment trap organic matter (Ward *et al.*, 2008; Babbin *et al.*, 2014; Chang *et al.*, 2014), and removal of all particles decreased rates of both anammox and denitrification (Ganesh *et al.*, 2015). Despite anammox bacteria being free-living organisms (Fuchsman et al., 2012; Ganesh et al., 2014), anammox rates correlate with particulate matter flux (Kalvelage *et al.*, 2013). This correlation likely arises because dissolved ammonium is typically < 10 nM in ODZs (Widner, Fuchsman, *et al.*, 2018; Widner, Mordy, *et al.*, 2018), and so anammox bacteria use ammonium produced in situ from organic matter remineralization (Devol, 2003). This dependence on remineralization of organic matter means that anammox rates should only be ~30% of the total N_2 production in modern ODZs (Devol, 2003). However, the presence of nitrite oxidation can short circuit denitrification, allowing a somewhat higher percentage (Penn *et al.*, 2016; Babbin *et al.*, 2020). In anoxic Proterozoic waters, ammonium may have been more widely available, preventing the tight coupling of anammox with organic matter.

Nitrate reduction can also lead to dissimilatory nitrate reduction to ammonium (DNRA). We note that DNRA is a process that removes nitrate, but since it produces ammonium, the net amount of fixed nitrogen does not change. DNRA is very important in coastal sediments under ODZs where it is mediated by giant sulfur bacteria and linked to S oxidation (Bohlen *et al.*, 2011; Dale *et al.*, 2016). The ammonium from DNRA can fuel anammox or photosynthesizers in the water column in these coastal systems (Lam *et al.*, 2009; Dale *et al.*, 2016; Michiels *et al.*, 2017). DNRA has been measured in the coastal ODZs (Lam *et al.*, 2009; Jensen *et al.*, 2011). However, in general DNRA seems to be unimportant in pelagic ODZs (Ganesh *et al.*, 2015; Fuchsman *et al.*, 2017; Zakem *et al.*, 2020) or in suboxic waters above sulfidic zones (Bonaglia *et al.*, 2016). The mechanisms to explain why DNRA is sometimes important compared to denitrification are not well understood, but culture work and energetic calculations indicate that denitrification is favored over heterotrophic DNRA if organic matter is limiting and DNRA is favored if nitrate is limiting (Strohm *et al.*, 2007). This relationship would be consistent with DNRA being found only in coastal ODZs, where organic matter concentrations are high. It may also suggest that DNRA was favored in the Proterozoic where nitrate levels were probably lower than today (Stüeken, 2013; Koehler *et al.*, 2017; Wang *et al.*, 2020). This view is supported by observations from a modern ferruginous lake where DNRA appears to be favored over denitrification and is stimulated by iron (Michiels *et al.*, 2017).

The effect of high iron concentrations on anoxic microbial communities

The ancient ocean was ferruginous, unlike the modern ocean where iron is usually at nanomolar to subnanomolar concentrations (Slemons *et al.*, 2010) even in offshore ODZs (Kondo and Moffett, 2013, 2015) though iron concentrations are higher when anoxic water overlies the continental shelf (Heller *et al.*, 2017; Scholz, 2018). Although the enrichment of iron in metalloenzymes found in ODZs likely reflect evolution in ferruginous conditions of the Archaean and Proterozoic (Glass *et al.*, 2015), present

conditions do not make ODZs a good proxy for iron cycling in the ancient ocean. A more appropriate modern analogue may be ferruginous lakes, which are sulfate poor (Crowe *et al.*, 2008). Photoferrotrophy is important in ferruginous lakes with miniscule sulfate concentrations where the light can reach the chemocline (Walter *et al.*, 2014; Llirós *et al.*, 2015; Camacho *et al.*, 2017; Thompson *et al.*, 2019). Specific green sulfur bacteria, purple sulfur bacteria, and purple non-sulfur bacteria can mediate photoferrotrophy (Camacho *et al.*, 2017). Cultures of purple sulfur bacteria have the highest rates of photoferrotrophy (Hegler *et al.*, 2008). However, green sulfur bacteria, both types using iron or reduced sulfur, can grow slowly at very low light levels (<50 lux; Hegler *et al.*, 2008; Marschall *et al.*, 2010). Thus different photoferrotrophs have different niches. A danger of photoferrotrophy for a pelagic microbe is that the microbe will become encrusted with iron and sink out of the water column (Thompson *et al.*, 2019). However, studied pelagic photoferrotrophs have a negative charge to their outer membrane, repelling the iron oxides, which typically have a negative surface charge (Thompson *et al.*, 2019). The organic matter from these photoferrotrophs can then support methanogenesis at depth (Thompson *et al.*, 2019), Interestingly, in anoxic lakes with even small sulfate and sulfide concentrations, anoxygenic photosynthesis with reduced sulfur is favored over photoferrotrophy (~1 µM reduced S; Crowe, Maresca, *et al.*, 2014). Thus, although photoferrotrophy may have been the main mechanism for driving iron oxidation in the Archean (Kappler and Pasquero, 2005; Crowe *et al.*, 2008; Butterfield, 2015; Camacho *et al.*, 2017; Schad *et al.*, 2019; Thompson *et al.*, 2019) where sulfate concentrations were low (perhaps as low as 2.5 µM; Crowe, Paris, *et al.*, 2014), photoferrotrophy was likely reduced in the Proterozoic where sulfate and reduced S were more plentiful (Scott *et al.*, 2014; Luo *et al.*, 2015). Additionally, the increase in cyanboacteria mediating oxic photosynthesis and the oxygen they produce would have pushed the photoferrotrophs deeper into the water column and further from light (Schad *et al.*, 2019).

Iron cycling at neutral pH is still being investigated in the modern day. Iron can definitely be microbially reduced using organic matter or sulfide under anaerobic conditions (Burdige, 1993). Ferric iron reduction can also be coupled to ammonium oxidation to N_2 (Fe-ammox) under high iron conditions (Li *et al.*, 2015, 2018; Stüeken *et al.*, 2016; Huang and Jaffé, 2018). On the other hand, reduced iron can be oxidized by microaerophilic iron oxidation (Singer *et al.*, 2011; Barco *et al.*, 2015; Chiu *et al.*, 2017). Anaerobic iron oxidation, formerly thought to be mediated by heterotrophic denitrifiers, may in fact be abiotic iron oxidation, driven by the nitrite that accumulated during denitrification (Klueglein and Kappler, 2013). This abiotic process appears to be important when ODZs overlap with the shelf and iron concentrations are elevated due to upward diffusion of iron from sediments into the oxygen-depleted water column, but may even occur to some extent offshore (Scholz *et al.*, 2016; Heller *et al.*, 2017). Additionally, there is one cultured example of anoxic chemosynthetic iron oxidizer that reduces nitrate, a betaproteobacteria (*Gallionellaceae*) (Straub *et al.*, 1996; He *et al.*, 2016; Tominski *et al.*, 2018). This culture reduces nitrate to nitrite and NO using iron, and other members of the community then reduce the NO to N_2 gas (He *et al.*, 2016). This iron mediated nitrate reduction has also been found in ferruginous lakes (Michiels *et al.*, 2017). Iron can also be oxidized by sinking manganese oxides, though this may be abiotic (Dellwig *et al.*, 2010). We would expect that under high iron conditions in the Proterozoic, iron would be microbially cycled through reduction using both organic matter and sulfide and oxidation using both oxygen, nitrate/nitrite, and photoferrotrophy. Similarly, oxidation of other metals, such as arsenic, may have contributed to chemoautotrophic nitrate reduction to nitrite (Saunders *et al.*, 2019). Arsenic was also at much higher concentrations in the Proterozoic ocean (Bergman and Kolesov, 2012; Fru *et al.*, 2015), and a complete arsenic redox cycle has been documented from ODZs even at modern low arsenic concentrations (Saunders *et al.*, 2019). Thus, in general, metal cycling may have been more important in the Proterozoic ocean than seen in modern ODZs.

Organic Matter

The nitrogen cycle is intimately linked to the carbon cycle because organic matter provides a possible reductant for nitrate and other oxidized forms of N, and because degradation of biomass releases

ammonium into the water column. In the modern ocean, much of the flux of organic matter to depth is dependent on eukaryotic organisms. Large phytoplankton aggregate and sink (Smetacek, 1985; Guidi *et al.*, 2009). Multicellular animals such as zooplankton or fish create fecal pellets that sink or swim to depth and deficate or excrete at depth (active transport) (Schnetzer and Steinberg, 2002; Steinberg *et al.*, 2002). Zooplankton also consume and fragment particles, mediating ~10% of carbon flux attenuation in the open ocean (Dilling and Alldredge, 2000; Stukel *et al.*, 2019). However, although eukaryotic algae first evolved in the Mesoproterozoic as coastal benthic species, they were marginalized until the Neoproterozoic, and the evolution of multicellular organisms occurred during the Neoproterozoic, perhaps due to higher oxygen concentrations (Butterfield, 2015). Protists that graze on bacteria had not yet evolved or were scarce during the Proterozoic (Butterfield, 2015) and some modern phytoplankton such as diatoms did not expand until the Mesozoic at which point the increasing sinking flux of organic matter may have contributed to further ocean oxygenation (Lu *et al.*, 2018). The lack of mulicellular animals or large shelled eukaryotic algae in the Proterozoic may have reduced fast sinking fluxes from surface waters compared to today, but without zooplankton, all the sinking flux that did occur would have been consumed by microbes or buried. However, mineral ballast is not necessary for export of organic matter from the euphotic zone (Thomalla *et al.*, 2008). Additionally, shelled organisms are not the only source of mineral ballast for sinking organic matter. Organic matter can pick up minerals such as carbonate or clay from the water column while sinking and these minerals causes the particles to be more dense and sink faster (Passow and De La Rocha, 2006). In cyanobacterial dominated oligotrophic waters, large particles appear to coalgulate from small (20-200 μm) particles right below the mixed layer rather than leaving the mixed layer as large particles (Cavan *et al.*, 2018).

The lack of protists does not necessarily mean that no predation occurred in the Proterozoic. In the present day, there are bacteria that predate on other bacteria. For example, *Bdellovibrio* enter the prey cell and consume it from the inside (Gophna *et al.*, 2006); *Myxococcus* stalk their prey and secrete bacteriolytic enzymes that lyse their prey bacteria (Hillesland *et al.*, 2007). These forms of predation are not nearly as efficient as the much larger filter feeding protists, however. Viruses, on the other hand, are thought to have evolved very early in Earth history (Hendrix *et al.*, 2000), and can infect species on a large scale. In general, viral lysis releases cell contents into the water column, which may be a particularly important source of organic matter for the surrounding microbial community (Fuhrman, 1999; Shelford *et al.*, 2012; Fang *et al.*, 2019). However, viral infections are thought to be able to terminate phytoplankton blooms causing particle formation (Brussaard *et al.*, 2005; Laber *et al.*, 2018; Sheyn *et al.*, 2018; Kranzler *et al.*, 2019). Viral infection causes cells to produce sticky materials and aggregate, and infected bacteria have been seen to clump together forming small particles (Shibata *et al.*, 1997). In the Eastern Tropical North Pacific ODZ, ODZ-specific cyanobacteria and their viruses were abundant on particles, implying the importance of viral infection on organic matter transfer in that system (Fuchsman, Palevsky, *et al.*, 2019). Thus, viral infection may have been an important source of organic matter in the Proterozoic.

In a further complication, since some complex organic carbon is resistant to degradation under anoxic but not sulfidic conditions (Van Mooy *et al.*, 2002), the scarcity of oxygen in the deep Proterozoic ocean would have limited respiration of organic carbon in the water column, which may have enhanced net export to the sediments (Van Mooy *et al.*, 2002; Keil *et al.*, 2016; Kipp and Stüeken, 2017). Overall, the mechanisms of the biological pump were different between the modern day and the Proterozoic, but transfer of organic matter to depth would still have occurred, providing reducing power and ammonium.

There is evidence of abundant phosphate and nitrate and large amounts of organic matter burial in the Paleoproterozoic (Bekker and Holland, 2012; Kipp and Stüeken, 2017; Kipp *et al.*, 2018). Presumably the ocean had rampant primary productivity and abundant organic matter fluxes during this time period. The Mesoproterozoic, on the other hand, is thought to have experienceed greatly reduced nitrate and phosphate levels and greatly reduced primary productivity and organic matter burial (Bekker and Holland, 2012; Kipp and Stüeken, 2017; Koehler *et al.*, 2017; Reinhard *et al.*, 2017; Crockford *et*

al., 2018). Thus we can broadly think of the Mesoproterozoic ocean as operating under oligotrophic conditions (Crockford *et al.*, 2018).

A large percent of the volume of modern oxygen deficient zones, especially in the Eastern Tropical North Pacific (ETNP), are under oligotrophic surface waters (Pennington *et al.*, 2006; Fuchsman, Palevsky, *et al.*, 2019). Primary productivity is low and cyanobacteria and tiny eukaryotic plankton such as green algae dominate surface waters in this region (Pennington *et al.*, 2006; Fuchsman, Palevsky, *et al.*, 2019). Rather than aggregates of large phytoplankton with mineral ballast sinking from surface waters, large particles in this region coalgulated from small (20-200 μm) particles right below the mixed layer (Cavan *et al.*, 2018), and fluxes from the surface waters are low (Cavan *et al.*, 2017; Fuchsman, Palevsky, *et al.*, 2019). N_2 production (by denitrification or anammox) is dependent on organic matter fluxes as heterotrophic denitrifiers directly utilize organic matter and anammox bacteria need the ammonium produced from organic matter degradation (Devol, 2003; Babbin *et al.*, 2014; Chang *et al.*, 2014; Ganesh *et al.*, 2015). However, despite low fluxes from surface waters, N_2 production occurs in the oligotrophic ETNP (Babbin *et al.*, 2014, 2015; Fuchsman, Palevsky, *et al.*, 2019).

One reason for this N_2 production under oligotrophic surface waters could be the supply of organic matter by active cyanobacteria in the ODZ at extremely low light levels (1% blue light; Cepeda-Morales *et al.*, 2009). In much of the Eastern Tropical North Pacific, a secondary chlorophyll maximum of low light adapted cyanobacteria photosynthesize inside the oxygen deficient zone providing organic matter straight to anaerobic bacteria (Cepeda-Morales *et al.*, 2009; Garcia-Robledo *et al.*, 2017; Fuchsman, Palevsky, *et al.*, 2019). ODZ cyanobacteria potentially provide up to 40% of the organic matter flux to the upper layer of the ODZ (Fuchsman, Palevsky, *et al.*, 2019) and provide oxygen to oxygen-utilizing microbes under anoxic conditions (Garcia-Robledo *et al.*, 2017). The presence of this cyanobacterial maximum in the ODZ is thought to be due to anoxic conditions preventing grazing on the cyanobacteria by oxygen-utilizing protists (Zakem *et al.*, 2020). Similarly, anoxygenic photosynthesis with reduced S can occur at sulfidic zone boundaries (Marschall *et al.*, 2010), or anoxygenic photosynthesis with reduced iron could occur under high iron conditions (Thompson *et al.*, 2019). When primary production, either by cyanobacteria or anoxygenic photosynthesis, occured in the anoxic waters of the Proterozoic, the resulting organic matter could have fuelled anaerobic microbial processes without the need to form sinking particles. Solar irradience was reduced during the Mesoproterozoic compared to modern day (Gough, 1981), which would have affected the depth range of photosynthetic organisms. Since the light needed for photosynthesis in the anoxic zone is dependent on shading from shallower organisms and the depth of the upper boundary of anoxic water, it is hard to know how much primary production occurred in anoxic waters of the Proterozoic, but, like the modern ocean, the presence of primary producers in anoxic waters likely varied with space and time (Marquez-Artavia *et al.*, 2019).

Photosynthesizers are not the only source of organic matter production under anoxic conditions. Additionally, above sulfidic zones, chemoautotrophic S-oxidizing bacteria can create an organic matter maximum at a sulfide interface (Glaubitz *et al.*, 2010; Kirkpatrick *et al.*, 2018; Scranton *et al.*, 2020). These S-oxidizing bacteria may be autotrophic denitrifiers using nitrate, or they may use oxygen (Glaubitz *et al.*, 2010; Kirkpatrick *et al.*, 2018). Productivity rates at these organic matter maxima at sulfide boundaries can rival rates in surface waters (Yilmaz *et al.*, 2006; Ediger *et al.*, 2019). The organic matter created at these interfaces sinks into the sulfidic zone (Scranton *et al.*, 2020) and thus fuels more sulfate reduction, leading to further organic matter recycling.

N cycling under suboxic/hypoxic conditions

Modelling and measurements have indicated that denitrification can occur inside particles under hypoxic conditions. N_2O production and reduction are 50% inhibited at 200 and 300 nM oxygen respectively (Dalsgaard *et al.*, 2014). However, there are oxygen gradients inside organic matter aggregates (Ploug *et al.*, 1997; Ploug, 2001; Ploug and Bergkvist, 2015). Inside particles in fully oxygenated seawater, oxygen utilization is generally not limited by the transport of oxygen into the

particle (Ploug, 2001). However, the potential for transport limitation of oxygen within particles, and therefore anoxia, is greatly dependent on particle size and ambient oxygen, with aggregates >1 mm being much more susceptible to anoxia (Klawonn *et al.*, 2015). In large aggregates, diffusion limitation of oxygen occurred below ambient O_2 concentrations of 100 µM (Ploug and Bergkvist, 2015; Stief *et al.*, 2016), and at ambient O_2 concentrations of 20 µM O_2, 50% of the interior of the aggregates became anoxic (Ploug and Bergkvist, 2015). In the marine environment, denitrification in aggregates, using N atoms originally from the particulate organic N and therefore oxidized in situ, has been detected at 30-50 µM ambient O_2 (Fuchsman, Paul, *et al.*, 2019). Global modeling of aggregates in the ocean has indicated that inclusion of denitrification inside particles in suboxic waters would double estimates of modern marine water column denitrification rates (Bianchi *et al.*, 2018). Thus, denitrification can occur in particles under suboxic conditions and with the same logic, sulfate reduction can occur in particles under nitrate conditions (Figure 2) and microbial evidence supports this idea (Fuchsman, Murray, *et al.*, 2012; Saunders *et al.*, 2019). We note, however, that in the modern ocean, particles created by picophytoplankton such as unicellular cyanobacteria are smaller than particles created by eukaryotic algae such as diatoms (Guidi *et al.*, 2009). Thus, particles in the Proterozoic could potentially have been small and thus less limited by diffusion. However, oxygen concentrations were also quite low, which may have counter-balanced this size-limitation.

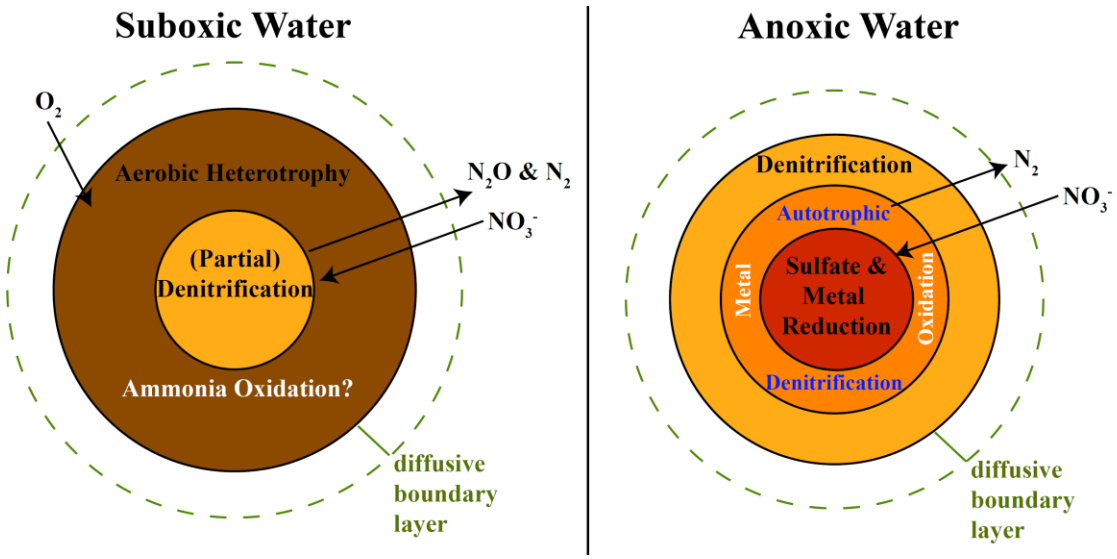

Figure 2: *Schematic of the processes occurring inside particles under suboxic and anoxic conditions. The dashed line indicates the particles's diffusive boundary layer.*

Suboxic waters may support oxic nitrogen cycling in the water column and denitrification in particles. The Bay of Bengal is a suboxic basin of the Indian Ocean with oxygen concentrations between 1-2 µM (Bristow *et al.*, 2017). Neither anammox nor denitrification rates were detected in the water column but nitrite oxidation rates were high (Bristow *et al.*, 2017). It has been suggested that nitrite oxidizers outcompete anammox for nitrite and/or ammonium under low oxygen (Bristow *et al.*, 2017; Penn *et al.*, 2019). 15N labeling, N_2O stable isotopes and modelling indicated that a large proportion of N_2O in the suboxic edge region above the ODZ is produced by denitrification (Babbin *et al.*, 2015; Ji *et al.*, 2015, 2018; Casciotti *et al.*, 2018). One theory to explain the production of N_2O from denitrification under suboxic conditions relates to small differences in the oxygen tolerance among steps in the denitrification pathway, with the last step being least tolerant (Babbin *et al.*, 2015). N_2O production by denitrification in these suboxic regions surrounding oxygen deficient zones may contribute 20% (0.5 Tg-N) of marine N_2O fluxes to the atmosphere (2.8 Tg-N) (Ji *et al.*, 2018). However, denitrifier genes were only found in the particle fraction, not in the water column in the suboxic edge region of the ODZ,

indicating that denitrification is particle-attached in these suboxic regions (Fuchsman *et al.*, 2017). These N_2O rate measurements (Babbin *et al.*, 2015; Ji *et al.*, 2015, 2018; Casciotti *et al.*, 2018) were all obtained from offshore regions dominated by cyanobacteria where, presumably, the particles were small. In the suboxic zone below the ODZ, where particle fluxes are reduced, stable isotopes indicate that ammonium oxidation was the primary N_2O source (Casciotti *et al.*, 2018).

Table 1: *Processes discussed in this paper compared between the modern and Proterozoic ocean. Cells indicate if these metabolisms are and were present in the suboxic (< 10 µM O_2) or anoxic (< 10 nM O_2) ocean.*

Process	Lifestyle	Modern suboxia	Modern anoxia	Proterozoic suboxia	Proterozoic anoxia	Implications
Archaeal ammonia oxidation	Autotroph	***Yes***[a]	No[a]	***No***	No	Possibly not yet evolved[b]
Bacterial ammonia oxidation	Autotroph	Black Sea but not ODZs[a,c]	No	***Yes***	No	Need higher [NH_4^+] and makes more N_2O than the archaea[d,e]
Nitrite oxidation	Autotroph	Yes	At least at periphery	Yes	At least at periphery	Produces nitrate. Uses O_2 at levels below which we can measure.[f]
Anammox	Autotroph	No (outcompeted)[g]	Yes	No (outcompeted)	Yes	N_2 producer
Heterotrophic denitrification	Heterotroph	In particles[h,i]	Yes	In particles	Yes	N_2 producer. Produces N_2O under suboxia.[j]
Denitrification w/S	Autotroph	No	Sulfidic Zone Boundary[k]	No	Sulfidic Zone Boundary	N_2 producer
Denitrification w/methane	Autotroph	No	***Low Levels***[l]	No	***Yes***	N_2 producer
Denitrification w/iron	Autotroph	No	***No***	No	***Yes***	Higher iron concentrations in Proterozoic
Fe-ammox	Autotroph	No	***Sediments***[m]	No	***Yes***	Higher iron concentrations in Proterozoic
DNRA	Heterotroph	No	Coastal[n]	No	Maybe[o]	Produces NH_4^+ Factors still unclear
DNRA w/S	Autotroph	No	Sulfidic sediments[p]	No	Sulfidic sediments	Not likely in water column[q]. Produces NH_4^+
Photoferrotrophy	Autotroph	No	***No***	No	***Yes***[r]	Needs light Produces organic C at redox boundary
Anoxygenic photosynthesis w/S	Autotroph	No	Sulfidic zone boundary[s]	No	Sulfidic zone boundary	Needs light Produces organic C at redox boundary
Oxygenic photosynthesis	Autotroph	Yes	Yes[t]	Yes	Yes	Needs light and nNo sulfide Produces organic C
Iron reduction	Heterotroph	No	Sulfidic zones	No	Sulfidic zones	Source of reduced iron

Differences are in bold italics.
[a]Peng *et al*. (2015).
[b]Ren *et al*. (2019).
[c]Lam *et al*. (2007).
[d]Martens-Habbena *et al*. (2009).
[e]Hink *et al*. (2017).
[f]Bristow *et al*. (2016).
[g]Bristow *et al*. (2017).
[h]Fuchsman *et al*. (2019a, 2019b).
[i]Fuchsman *et al*. (2017).
[j]Babbin *et al*. (2014).
[k]Hannig *et al*. (2007).
[l]Thamdrup *et al*. (2019).
[m]Li *et al*. (2015).
[n]Lam *et al*. (2009).
[o]Michiels *et al*. (2017).
[p]Bohlen *et al*. (2011).
[q]Bonaglia *et al*. (2016).
[r]Thompson *et al*. (2019).
[s]Marschall *et al*. (2010).
[t]Garcia-Robledo *et al*. (2017).

50% of the ocean may have been suboxic during the Mesoproterozoic (Reinhard *et al.*, 2013), and surface water oxygen levels were likely high enough to efficiently oxidize ammonium and nitrite to nitrate (Bristow *et al.*, 2016; Hardisty *et al.*, 2017). However, the rock record indicates that nitrate concentrations were low in offshore waters (Koehler *et al.*, 2017), which means that nitrite and nitrate did not accumulate, but were rapidly assimilated or re-reduced to N_2 or ammonium at the chemocline within accumulating organic particles. Larger particles form from physical aggregation of smaller particles below the mixed layer in parts of the modern ocean dominated by cyanobacteria and microalgae (Cavan *et al.*, 2018). Presumably a similar process would provide particles to the deeper Proterozoic ocean. In Proterozoic suboxic waters, denitrification may have been confined to particles, whereas anammox, a free-living process, would perhaps have been relatively unimportant (Figure 3). The amount of denitrification in these suboxic waters would have depended on organic matter availability and likely on particle size, which are difficult to predict accurately. The largest difference in the suboxic microbial community between the Proterozoic compared to modern suboxic waters was likely the dominance of bacterial ammonium oxidizers, which have higher half saturation constants for ammonium and produce

more N_2O than modern ammonia oxidizing archaea (Goreau *et al.*, 1980; Martens-Habbena *et al.*, 2009; Kozlowski, Kits, *et al.*, 2016; Hink *et al.*, 2017) (Table 1). Partial denitrification in particles and bacterial ammonium oxidation in the water column would likely produce N_2O under these conditions (Figure 2 and 3). The interfaces of these suboxic waters, including particles, would also promote microaerophilic metal oxidation (Clement *et al.*, 2009; Barco *et al.*, 2015).

Nitrogen cycling in anoxic waters

In modern oxygen deficient zones, where oxygen is below 10 nM (Revsbech *et al.*, 2009) and sulfide is not detectable, N cycling is closely linked to organic matter fluxes. Denitrification is dependent on organic matter (Ward *et al.*, 2008; Babbin *et al.*, 2014; Chang *et al.*, 2014) (Ganesh *et al.*, 2015), and anammox bacteria use ammonium produced from organic matter remineralization (Devol, 2003) (Ganesh *et al.*, 2015). Nitrate reduction to nitrite is the dominant rate process in the anoxic water column (Lam *et al.*, 2009), with ~80% of the microbes present containing nitrate reduction genes in the ETNP (Fuchsman *et al.*, 2017). However, nitrate reduction is heterotrophic and nitrate reduction rates are still linked to organic matter fluxes (Ganesh *et al.*, 2015). In the ETSP and ETNP oxygen deficient zones, denitrification genes as a whole were enriched in the particulate fraction compared to free-living fraction (Ganesh *et al.*, 2014, 2015; Fuchsman *et al.*, 2017) though at least one denitrifier specialized in the ODZ water column rather than particles (Fuchsman *et al.*, 2017). Low levels of autotropic dentrification with methane have also been detected in an oxygen deficient zone (Thamdrup *et al.*, 2019). Cryptic sulfate reduction and S-oxidizing autotrophic denitrification was found in the coastal ETSP and proposed to be due to more reducing conditions in particles (Canfield *et al.*, 2010; Stewart *et al.*, 2012). Additionally, S-oxidizing denitrifiers as well as sulfate reducers were identified as particle-attached in the offshore ETNP ODZ and in the suboxic but not sulfidic water column of the Black Sea (Fuchsman, Murray, *et al.*, 2012; Fuchsman *et al.*, 2017; Saunders *et al.*, 2019). However, the majority of denitrification in oxygen deficient zones is heterotrophic (Fuchsman *et al.*, 2017; Thamdrup *et al.*, 2019). N_2O concentrations in oxygen deficient zones are some of the lowest in the ocean because N_2O is consumed by the denitrifiers under anoxic conditions (Casciotti *et al.*, 2018).

The Proterozoic deep ocean is thought to have been at least 30-40% and possibly up to 100% anoxic (Reinhard *et al.*, 2013). In the Paleoproterozoic, abundant organic matter and nitrate would likely have stimulated massive N_2 production by denitrification. The importance of anammox would have depended on the availability of ammonium, which was probably high due to extensive decay of abundant organic matter within sediments and in the water column. In Mesoproterozoic oxygen deficient waters, geochemical data suggest that organic matter and nitrate were much less abundant (Bekker and Holland, 2012; Kipp and Stüeken, 2017; Koehler *et al.*, 2017; Reinhard *et al.*, 2017; Crockford *et al.*, 2018). Since nitrate could have been limiting, the ability of bacterial ammonium oxidizers to oxidize ammonium at low oxygen concentration could have been critical to this ecosystem. As nitrate reduction and dentrification are generally fueled by organic matter, rates of active N cycling were likely highest at the top of the oxygen deficient waters where organic matter fluxes from surfaces waters were greatest or where primary producers (cyanobacteria or anoxygenic photosynthesizers) could have been present. Anammox was also likely linked to ammonium production from this organic matter remineralization. Nitrate reduction can lead to either N_2 production by denitrification/anammox or ammonium production by DNRA. High rates of DNRA have been measured in ferroginous lakes, greatly promoting productivity there (Michiels *et al.*, 2017). It is unclear how important DNRA was in the Proterozoic ocean. Heterotrophic DNRA is not favored under the low organic matter conditions (Strohm *et al.*, 2007) found in the Mesoproterozoic (Bekker and Holland, 2012; Kipp and Stüeken, 2017; Koehler *et al.*, 2017; Reinhard *et al.*, 2017; Crockford *et al.*, 2018) and S oxidizing DNRA was not found at the sulfide interface of the Baltic Sea (Bonaglia *et al.*, 2016). However, in the more productive Paleoproterozoic (Bekker and Holland, 2012; Kipp and Stüeken, 2017; Kipp *et al.*, 2018), DNRA could have been more important.

Some potentially large differences between the anoxic Proterozoic ocean and modern ODZs could be a greater importance of biological nitrate reduction with iron, Fe-ammox and of autotrophic denitrification with methane (Table 1). Due to higher concentrations of iron and some other metals, nitrate reduction from iron oxidation as well as from other metals such as arsenic likely occurred in this system (Straub *et al.*, 1996; Scholz *et al.*, 2016; Saunders *et al.*, 2019). In these cases, ammonium from organic matter respiration would not be formed. Fe-ammox where ammonium is oxidized with iron oxides could also have occurred *(Li et al., 2015, 2018; Stüeken et al., 2016; Huang and Jaffé, 2018)*. The importance of autotrophic denitrification with methane in the anoxic waters of the Proterozoic would depend on the concentration of methane and nitrate in the ocean. The flux of methane from marine sediments during the Mesoproterozoic is predicted to be twice modern levels (Bjerrum and Canfield, 2011; Roberson *et al.*, 2011). However, methane can also be oxidized anaerobically by sulfate, manganese oxides and iron oxides (Beal *et al.*, 2009), which would all have been present in the Proterozoic. Autotrophic denitrification with methane is likely to have been more important in the Proterozoic than today, but is unlikely to be a dominant process.

Nitrogen cycling in sulfidic waters

The Baltic and Black Seas are meromictic basins that can be used as analogs for sulfidic marine margins in the Proterozoic ocean. In the Baltic Sea, where conditions are changeable due to periodic flushing with oxic waters, S-oxidizing autotrophic dentitrification dominates N_2 production whenever nitrate concentrations overlap with the sulfidic zone and anammox has dominated when sulfide and nitrate do not overlap (Hannig *et al.*, 2007). S-oxidizing autotrophic denitrification has also been identified during a sulfidic event on the Namibian shelf (Lavik *et al.*, 2009). Under modern conditions, large concentrations of N_2O are not produced during S-oxidizing autotrophic denitrification because N_2O is consumed by the denitrifiers (Lavik *et al.*, 2009). In the Black Sea, a stable meromictic basin where nitrate concentrations in surface waters are quite low (3-5 μM compared to >20 μM in modern ODZs; Fuchsman *et al.*, 2008), nitrate and sulfide do not overlap. Sinking manganese oxides may separate oxygen and nitrate from sulfide in the Black Sea by consumption of oxygen in manganese oxide formation and consumption of sulfide in reaction with the sinking manganese oxides (Yakushev *et al.*, 2009). The reduced manganese then diffuses upward and is reoxidized. These manganese oxides also oxidize iron as they sink, forming particles with both iron and phosphorus (Dellwig *et al.*, 2010). Not only do these metal containing particles separate nitrate and sulfide, when they also coagulate with organic matter, they provide habitat for metal and S cycling microbes (Fuchsman *et al.*, 2011; Fuchsman, Murray, *et al.*, 2012).

In the Black Sea, ammonium upwelling into the suboxic zone from the sulfide zone can be oxidized to nitrite at very low oxygen concentrations, potentially by gammaproteobacterial ammonia oxidizers, and this nitrite can be used by anammox bacteria (Lam *et al.*, 2007). Thus this upward flux of ammonium allows N_2 production from anammox to occur consistently without regard to organic matter flux from surface waters (Fuchsman, Staley, *et al.*, 2012; Kirkpatrick *et al.*, 2012). Anammox bacteria were even found to be active in the upper sulfidic zone (< 10 μM H_2S; Kirkpatrick *et al.*, 2012). However, in this system heterotrophic dentrification is still linked to high organic matter fluxes (Kirkpatrick *et al.*, 2012; Fuchsman, Paul, *et al.*, 2019). Thus, low oxygen waters above sulfidic regions have many potential sources of N_2 production.

In areas of the Mesoproterozoic ocean where sulfide was present, anammox or autotrophic denitrification may have dominated, depending on the overlap of nitrate with dissolved sulfide. As nitrate concentrations were low in offshore waters in the Mesoproterozoic (Koehler *et al.*, 2017), it seems likely that, like in the Black Sea, aerobic ammonium oxidation would utilize the consistent upward flux of ammonium from the sulfide zone to make nitrite and that anammox would use this nitrite and the upward flux of ammonium to dominate N_2 production above offshore sulfidic waters (Figure 3). In this situation, nitrite is produced but does not accumulate. S-oxidizing autotrophic denitrification would likely have

been more prevalent at the sulfide interface in coastal regions, where both nitrate and metal concentrations were likely more abundant (Figure 3).

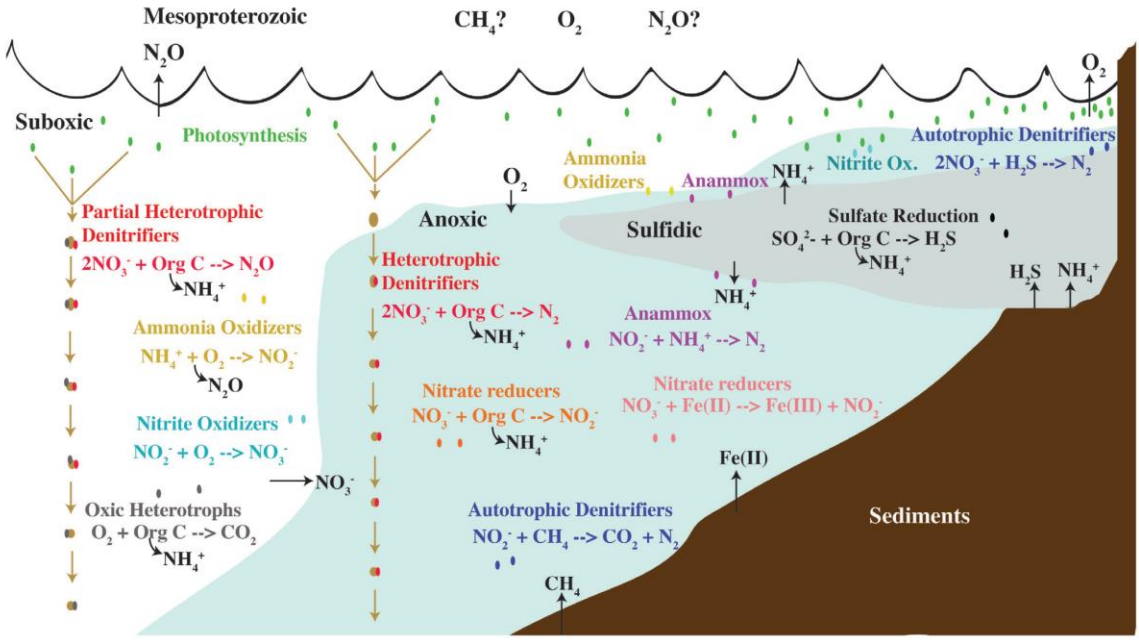

Figure 3: *Schematic of microbial ecosystem during the Mesoproterozoic with sulfidic water in gray, anoxic water in blue, and suboxic water in white. Microbes are ovals that are colored similarly to the name of the process they represent. These ovals indicate whether these processes would occur on particles or the water column or at redox interfaces. Arrows indicate diffusion out of sediments, between redox zones, or to the atmosphere.*

N_2O and the Proterozoic Ecosystem

Solar luminosity was 83% of current levels during the early Proterozoic and increased to 95% over that billion year time period (Gough, 1981). However, the absence of glacial deposits indicates that global temperatures were temperate during the Mesoproterozoic (Crowell, 1999). About 10°C of additional warming would have been needed to maintain ice-free conditions in the Mesoproterozoic (Roberson *et al.*, 2011). Four greenhouse gases have the potential to cause this warming: CO_2, CH_4, N_2O and H_2O. For CO_2 to be the sole greenhouse gas warming the Proterozoic atmosphere, 100 times modern levels of CO_2 would be necessary (Kasting, 1987), and the amount of atmospheric CO_2 would have to decrease as the Sun's intensity increased. The constant isotopic composition of both carbonate and organic carbon throughout the Mesoproterozoic is inconsistent with CO_2 levels declining with time (Shields and Veizer, 2002; Buick, 2007). Additionally, the use of carbon dioxide concentrating mechanisms by cyanobacteria at 1.2 Ga indicate that carbon dioxide levels were not excessive during the Mesoproterozoic (Kah and Riding, 2007). Thus the presence of another greenhouse gas is necessary. Models indicate that the development of a UV-shielding ozone layer allowed some methane to be photolytically stable in the oxygenated Mesoproterozoic atmosphere (Claire *et al.*, 2006). However, models of the Proterozoic biogeochemistry fail to produce enough methane to warm the atmosphere, because methane is rapidly consumed by sulfate reducing bacteria (Olson *et al.*, 2016). Further, depleted $\delta^{13}C_{org}$ values indicative of high marine methane concentrations in the rock record are not widespread (Shields and Veizer, 2002; Buick, 2007). It has been suggested that a terrestrial source of methane may solve this problem (Zhao *et al.*, 2018), but observational evidence for this hypothesis is so far limited to the Archean (Flannery *et al.*, 2016; Stüeken and Buick, 2018). Models with both methane and N_2O jointly warming the atmosphere have been proposed (Roberson *et al.*, 2011).

Two alternative sources of N_2O during the Mesoproterozoic have been considered. Buick (2007) argued that low copper concentrations in seawater limited the final step of heterotrophic denitrification in anoxic waters created an additional N_2O flux, allowing N_2O to be a key greenhouse gas in the Mesoproterozoic. The nitrous oxide reductase enzyme (Nos), which catalyses this step contains twelve copper atoms in its active site (Haltia *et al.*, 2003). Experiments with denitrifying cultures have shown that copper-limited cultures of denitrifiers undergo incomplete denitrification at 10^{-15} M Cu (Granger and Ward, 2003; Twining *et al.*, 2007). Copper precipitates in the presence of sulfide, leaving the water column depleted in dissolved copper, which supports a model of low Proterozoic Cu levels. However, copper to titanium ratios over time do not show a decrease in copper concentrations during the Mesoproterozoic (Fru *et al.*, 2016), making copper limitation of nitrous oxide reductase unlikely. Due to high iron concentrations in the Archaean and Proterozoic, abiotic chemodenitrification with iron, a process which predominately produces N_2O not N_2, has been suggested as a N_2O source during the Mesoproterozoic (Stanton *et al.*, 2018). Kinetic calculations indicate the possibility of this process in the Mesoproterozoic (Stanton *et al.*, 2018), but more precise estimates of past nitrate and iron concentrations are needed to test if this N_2O source would have been significant.

In the modern ocean, our understanding of the mechanisms creating N_2O under low oxygen conditions has recently improved by the discovery that partial denitrification in particles is a significant source of N_2O under suboxic conditions (Babbin *et al.*, 2015; Ji *et al.*, 2015). In the modern ocean, 0.5 Tg of the 3 Tg-N total N_2O atmospheric fluxes is produced by partial denitrification in particles under suboxic water column conditions (Ji *et al.*, 2018), which compose 7% of the modern ocean (Paulmier and Ruiz-Pino, 2009). Other marine N_2O fluxes come from ammonium oxidation under low oxygen conditions. Since 50% of the ocean may have been suboxic during the Mesoproterozoic, simple scaling from 7% to 50% would imply that significant N_2O fluxes (~20 Tg) from suboxic waters to the atmosphere likely occurred during that time period. However, models indicate that 40 Tg N_2O were needed to support even 3^{o}C of warming (with methane providing the remaining warming needed) (Roberson *et al.*, 2011). Thus partial denitrification under suboxic conditions is unlikely to produce enough N_2O to substantially warm the atmosphere of the Mesoproterozoic. The importance of N_2O as a greenhouse gas in the Mesoproterozoic remains unclear.

Conclusions

Although a billion years of evolution has occurred since the Mesoproterozoic, including the evolution of single celled eukaryotic algae and multicellular organisms, the majority of microbial biogeochemical pathways, except archaeal ammonia oxidation, had already evolved by that time. The largest difference between the Proterozoic ocean and modern low oxygen marine systems were the high iron concentrations in the Proterozoic. In general, nitrate reduction and perhaps autotrophic denitrification from iron oxidation could have been a much more important process in the Proterozoic. Despite that, both heterotrophic and autotrophic pathways of the N cycle fundamentally depend on organic matter availability and remineralization. From microbially dominated photosynthesizers, low organic matter export fluxes are likely but not necessary. However, we note that organic matter production by oxic photosynthesis under low light or by anoxygenic photosynthesis using iron or reduced S can create important sources of organic matter directly in low oxygen waters, fueling N_2 production and closing the N cycle. Additionally, partial denitrification inside sinking organic matter in suboxic waters, ammonia oxidation by bacteria, and potentially abiotic iron oxidation were likely important N_2O sources to the atmosphere.

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